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THE INTERACTIONS OF CELLULOSE ACETATE
AND ETHYL CELLULOSE INHIBITORS WITH
DOUBLE-BASE PROPELLANTS

R. Stenson

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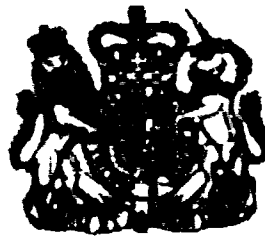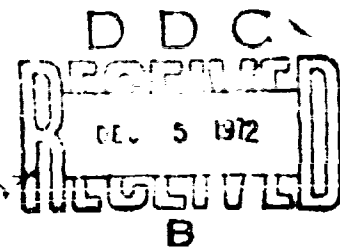Establishment
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The Interactions of Cellulose Acetate and Ethyl
Cellulose Inhibitors with Double-Base Propellants

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SUMMARY

The interactions of nitroglycerine in double-base propel-
lants with the inhibition materials cellulose acetate and
ethyl cellulose are described.   The distribution of nitro-
glycerine within the inhibitor and the effects of time,
temperature, nitrocellulose content of the propellant,
barrier layers and fillers on rates of absorption are
covered.   Reference is made to methods of bonding ethyl
cellulose to propellant.

Finally the investigations are extended to a range of
polymers which are possible inhibitors, and also to a
number of plasticisers likely to be present.

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FOREWORD

This paper by Dr R Stenson was originally written for the
Annual Meeting of the Institut für Chemie der Treib-und
Explosivstoffe held at Karlsruhe in September 1971.

This paper is now reproduced as an ERDE Technical Note in
order that somewhat wider circulation can be given.

IV

1 INTRODUCTION

An important physical factor which can affect the Service Life of a solid propellant rocket motor is the extent of migration of ingredients within the rocket motor, particularly when the propellant or other components contain low molecular weight ingredients such as plasticisers and stabilisers capable of diffusing rapidly under hot storage conditions. Ingredient migration is a particularly difficult problem for double-base propellants where absorption of nitroglycerine by the insulant or inhibitor can affect propellant ballistics, and increased combustion of the inhibitor may be serious enough to cause "burn-through" and expose a larger propellant surface area than was intended. Swelling of the insulant or inhibitor due to plasticiser absorption can occur and cause high stress concentrations at sharp corners, particularly for thermosets, with consequent bond failures. The inhibitor may also become mechanically weak and softened due to plasticiser absorption. In extreme cases the storage life of the rocket motor can be limited severely by motor failure on firing due to nitroglycerine diffusion and not by an inherent limitation on the life of the propellant charge. Experiments conducted at ERDE to classify migration parameters are described in this paper.

2 TESTING OF INHIBITION MATERIALS

2 1 "Sandwich" Tests

The extent of plasticiser absorption for an inhibitory material is determined on a laboratory scale by sandwiching a sample of polymer 25 mm square x 2.5 mm thick between two 25 mm squares of the propellant under investigation and determining weight changes with time of hot storage. For those materials which absorb large amounts of nitroglycerine (eg cellulose acetate) it is advisable to choose the propellant thickness about five times that of the inhibitor. Good surface contact is ensured by placing a 200 g weight on top of the sandwich and to minimise plasticiser loss to the atmosphere the assembly is enclosed in an inverted aluminium beaker resting on an aluminium dish. The polymer is removed at convenient time intervals and weighed. The rate of increase in weight is high initially but gradually decreases until equilibrium is approached. The nitroglycerine content of the inhibitor is determined polarographically at the end of test. The weight gain is expressed as a per cent of the original weight of inhibitor and for comparison the nitroglycerine analysis is converted similarly, but this is only strictly valid if no other complicating migrations occur. If inert plasticiser is lost from the inhibitor then the nitroglycerine absorption may be significantly higher than the weight gain. A separate control square of inhibitor is hot stored under similar enclosed conditions, weighed for loss of plasticiser to the atmosphere and a correction factor is applied to all sandwich test weights. The time to maximum weight increase is longer for thicker samples of inhibitor and comparisons must be made at constant thickness. Typical results for three conventional inhibitors and two double-base propellants plasticised with different amounts of nitroglycerine are given in Table 1.

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TABLE 1

Polymer	Sandwich Test 60°C		
	Propellant	Inhibitor	
	Nitroglycerine content, per cent	Maximum weight increase, per cent	Nitroglycerine content, ᵖer cent
Plasticised cellulose	48	100	95
acetate	43	88	87
Plasticised ethyl	48	17	14
cellulose	43	15	19.6
Filled flexible crosslinked	48	38	36
polyester	43	27	30

Plasticised cellulose acetate has been used extensively for the inhibition of
the larger double-base propellant charges.   Its disadvantages are well known
and tend to outweigh its ready availability, cheapness, ease of fabrication
and ability to adhere strongly to propellant surfaces.   It has been replaced
in current rocket motors employing cast propellants where the plasticiser
content of the propellant approaches 50 per cent since migration of nitro-
glycerine to the inhibitor is unacceptably high.   The nitroglycerine
absorptions observed in the sandwich test are broadly in line with those
found for inhibitor stripped from charges after storage.

Ethyl cellulose has been used as an alternative for loose extruded propellant
charges in some applications since it is less affected by nitroglycerine.
It has not been universally adopted since there are difficulties in bonding
in the cast double-base process, its low softening point has precluded its
use in long burning time cigar-burning charges and there are difficulties of
supply in the UK.   Recent work on the adhesion of ethyl cellulose has been
reported by the author's laboratory.[1] Epoxy resins and solutions of ethyl
cellulose dissolved in suitable solvents will bond the inhibitor to a
propellant surface but difficulties still exist in cast double-base applica-
tions although pre-treatment of the ethyl cellulose by etching shows some
improvement and merits further investigation.

A filled flexible crosslinked polyester has intermediate absorption character-
istics.   The interactions and cross migrations of inhibitor constituents,
propellant plasticisers and stabilisers were examined in detail for a double-
base propellant inhibited with filled polyester stored at 60°C.   Wet
exudation, observed on the exterior of the inhibitor, was found to contain
about 40 per cent nitroglycerine with polyester diluent.   The inhibitor was
removed from the charge after 6 months storage and found to have absorbed

25 per cent nitroglycerine. An inhibitor of this type is inferior to ethyl cellulose but its ease of application may have some attraction for special purposes.

The effect of increasing the storage temperature is to increase the rate of nitroglycerine diffusion and to reduce the time to equilibrium. The prediction of storage lives of rocket motors from accelerated testing, to the point where the nitroglycerine content of the inhibitor becomes critical, requires both a knowledge of reliable temperature coefficients of diffusion for each increment of temperature and also data on the firing capability in a particular design of rocket motor with varying degrees of migration. The temperature coefficient per $10^{\circ}C$ for time to absorb a known amount of nitroglycerine and time to equilibrium for cellulose acetate is taken as 2.0, but the experimentation is not conclusive and various figures have been reported. For standard inhibitors a nitroglycerine absorption of 20 to 25 per cent is regarded as highly detrimental.

The migration of nitroglycerine can be reduced by several techniques involving both propellant and inhibitor modifications. Reducing the plasticiser and increasing the nitrocellulose content of the propellant will obviously decrease the rate of migration and the final concentration of nitroglycerine in the inhibitor. Fig 1 highlights the magnitude of the advantage of using hard propellants.

In order to use a soft highly plasticised propellant, the interposition of a barrier film resistant to nitroglycerine, between the cellulose acetate and the propellant may be essential. Most barriers absorb a small amount of nitroglycerine and are not completely impermeable to plasticiser, but Fig 2 illustrates that the storage life can be increased by at least fivefold for approximately 25 per cent nitroglycerine absorption and the final concentration can be halved. For rubbery barrier layers, generally, there are no problems but for thinner non-rubbery barriers bonding and mis-match of mechanical properties with the propellant require careful attention.

Alternatively the storage life may be increased by the incorporation of relatively non absorbing fillers into the cellulose acetate. Fig 3 shows that the final overall extent of nitroglycerine migration is reduced slightly more than pro rata with increase of filler content. The final concentration of nitroglycerine absorbed by the cellulose acetate matrix is 60 to 70 per cent compared with 81.5 per cent for the unfilled inhibitor. The reinforcement and reduced ablation conferred by a suitable filler can give a bonus in increasing "burn-through" time, and the storage life is likely to be improved markedly.

2 2   Testing of Inhibited Charges

The sandwich test is a useful laboratory aid but the results must be corroborated by tests on actual rocket propellant charges. Diffusion processes are complex and plasticisers present in the inhibitor will also migrate into the propellant. The distributions of nitroglycerine and plasticisers on both sides of the propellant/inhibitor interface were determined at ERDE by Scrivener and Stacey. Experimentally two test assemblies were used. A cellulose acetate or ethyl cellulose disc 1.7 mm

thick was sealed with adhesive to the end of a solid cylindrical section of double-base propellant (length 50 mm, diameter 28 mm). The specimen was then placed on its unrestricted end in a closed container and stored at 54.5°C for the required period. Successive layers of inhibitor were turned off on a lathe; the nitroglycerine content of each layer was determined polarographically and the plasticiser by infra-red analysis. In the second test rocket propellant charges 500 mm long x 45 mm diameter were inhibited by the stress relief process and stored relatively unconfined at 54.5°C. Short lengths of propellant were removed for analysis, the end 25 mm being rejected in each case. Again layers of inhibitor were removed as before for analysis.

Results for end-inhibited specimens are shown in Figs 4, 5 and 6. The higher concentration of nitroglycerine in cellulose acetate than in ethyl cellulose throughout the inhibitor was confirmed but the distribution was not uniform in the early stages of storage. The time required to attain equilibrium depended on the extent of nitroglycerine absorption; between 4 and 11 weeks for ethyl cellulose and between 11 and 26 weeks for cellulose acetate. The relatively higher nitroglycerine content of the outer layers of ethyl cellulose before equilibrium indicated that in addition to the diffusion process some absorption of nitroglycerine vapour had occurred. The equilibrium concentration of nitroglycerine was 47 per cent total weight for cellulose acetate which agrees with the result by sandwich test of 87 per cent when calculated on the basis of original weight, assuming no inert plasticiser migration. Results for ethyl cellulose were similar to those derived from sandwich tests. Migration into the inhibitor created a propellant surface layer deficient in nitroglycerine to a depth of at least 4 mm from the interface. This was particularly evident for cellulose acetate.

The reason for the abnormally high concentration of nitroglycerine at a depth of 0.5 mm from the interface in the propellant inhibited with ethyl cellulose is probably associated with the coating cement employed, but a more detailed analysis of this region is necessary to understand the phenomenon.

Comparison of results with the nitroglycerine distribution data obtained from inhibited charges (Figs 8, 9 and 10) shows that loss of nitroglycerine to the atmosphere occurred in unconfined storage conditions since equilibrium was not attained in the inhibitor after 26 weeks. A reduced nitroglycerine content in the surface layers of the propellant was also evident.

Inert plasticiser in the inhibitor or residual solvent from the coating cement also migrated readily into the propellant (Figs 7 and 11). Ethyl cellulose originally contained 8 per cent total weight of phthalate esters which migrated to a depth of at least 4 mm into the propellant until the final concentration was about 4 per cent in both inhibitor and propellant. Cellulose acetate originally contained 12.4 per cent triacetin and 7.1 per cent total weight triphenyl phosphate. Again plasticiser migration was extensive.

2 3   Liquid Absorption Tests

Polymer/Nitroglycerine Interactions

Since the duration of the sandwich test is similar to that for the stored
rocket charge at elevated temperatures, a more rapid general screening test
has been adopted at ERDE to increase understanding of plasticiser migration.
A sample of the polymer 2.5 mm thick was suspended fully immersed in the
liquid plasticiser in a sealed tube.   The sample was removed at suitable
time intervals, dried on a filter paper and reweighed.   Whilst this method
does not reproduce conditions of storage of inhibited charges, a useful
order of merit of polymer absorption characteristics has been made.   The
method also has the advantage that the maximum plasticiser absorption for
a given polymer is found and this represents an upper limit which cannot be
exceeded in practical rocket motors.

For safety reasons nitroglycerine was diluted with 24 per cent triacetin
before use and 1 per cent stabiliser was included.   Weight increases were
then attributable to absorption of both plasticisers and separate experiments
using 100 per cent triacetin were necessary to resolve the contribution
played by nitroglycerine.   When necessary the polymer can be analysed for
nitroglycerine absorption.   Generally however triacetin, although slightly
more active in some systems, behaved similarly to nitroglycerine so that the
behaviour of nitroglycerine could be inferred with reasonable certainty.

The relative order of merit determined by the sandwich test is confirmed in
the liquid absorption test but the interaction between polymer and plasti-
ciser is considerably greater.   Cellulose acetate dissolved in both
liquids and gave a viscous solution so that measurements were obviated.   The
filled flexible polyester absorbed 70 per cent nitroglycerine/triacetin
mixture and 52 per cent triacetin.   Swelling of the sample was evident and
it was found that the weight per cent increase due to absorption of
plasticiser was approximately equal to the per cent volumetric swelling.
Consequently 25 per cent absorption by the inhibitor on a double-base
propellant charge would involve considerable stresses at the interface.
Ethyl cellulose absorbed 17 per cent mixed plasticiser which was found on
analysis to be largely nitroglycerine.

Results for a range of rubbers, thermosets and thermoplastics are given in
Table 2.   The behaviour of a number of the materials was confirmed by
absorption in contact with propellant plasticised with nitroglycerine.

Generally polymers of low polarity resisted nitroglycerine whereas highly
polar polymers were plasticised.   A reduction in the mobility of the
polymer chains either by crosslinking, or by a high degree of crystallinity
(linear thermoplastics) was accompanied by a marked reduction in the ability
of the nitroglycerine molecules to diffuse.

The potential of polymers absorbing low amounts of plasticiser is promising,
but those listed in Table 2 may or may not be suitable depending upon other
desiderata.

TABLE 2

ABSORPTION BY POLYMERS OF NITROGLYCERINE

Low Less than 10 per cent	Moderate 10 to 20 per cent	High 20 per cent and over
*Polyolefine Substituted Polyolefine Polyolefine copolymers Modified polyvinyl acetate copolymer *Crosslinked polyolefine (CP) Modified polyolefine copolymer *Elastomer A (EA) *Rigid Polyesters (PR) Rigid epoxides Rigid polyvinyl chlcride Butyl rubber *Carboxy-terminated polybutadiene (CTPB) Polymer No 1 Neoprene Polystyrene Polyamide	*Ethyl cellulose (EC) Flexible epoxide CTPB Polymer No 2	*Cellulose acetate (CA) *Very flexible polyesters (PVF) *Filled flexible polyester (PFF) Nitrile rubber Acrylonitrile butadiene styrene copolymer *Polyurethane rubber (PU) Elastomer B

*Behaviour in triacetin alone also tested.

Polymer Interactions with Other Propellant Ingredients

Liquid absorption tests were also carried out to examine the diffusion into polymers of other liquid nitric ester and non-explosive plasticisers encountered in double-base and composite propellants.   Diethylene glycol dinitrate (DEGN) was examined since it has been used in some double-base propellants.   Triethylene glycol dinitrate (TEGN) was also tested since it has been used in double-base and some composite propellants.   Results for plasticiser absorption, together with those for triacetin, a standard double-base propellant plasticiser, are given in Table 3.

The trend of behaviour with DEGN and TEGN is similar to that of nitro-glycerine and triacetin with only minor differences in the absolute level of plasticiser absorption in most cases. Polymers which are acceptable in contact with nitroglycerine are likewise generally acceptable for propellants containing the alternative nitric esters. The temperature coefficient of time to maximum absorption is generally about 1.6 to 2.0/10°C. The extent of plasticiser absorption is not independent of temperature for some systems and reverse migration on cooling of rocket motors after hot storage may be a complicating factor.

TABLE 3

Plasti-ciser	Weight per cent Absorption of Plasticisers by Polymers at 50°C								
	CA	EC	PVF	PFF	PR	CP	PU	EA	CTPB
Nitro-glycerine/Triacetin	S	17(16)	S	70(35)	6 (7)	4(4)	65(50)	0(1)	16(10)
Triacetin	S	40 (-)	S	52 (-)	3 (-)	4(-)	100 (-)	0(-)	6 (-)
DEGN	200(200)	28(25)	S	50 (-)	25(26)	5(2)	70 (-)	0(1.5)	4 (4)
TEGN	130(130)	18(25)	S	59(61)	20(22)	5(5)	70(50)	0(1.5)	3 (4)

S = dissolved
( ) = nitric ester analysis

The behaviour of dibutyl phthalate used in double-base propellants and isodecyl pelargonate used in some composite propellants was also tested; results are given in Table 4.

The behaviour pattern of the longer chain non-explosive plasticisers is different to triacetin and the nitric esters and the order of merit in Table 2 is frequently reversed. The interactions of DBP and IDP are not necessarily similar; for example migration from composite propellants containing IDP to elastomer A and DBP from double-base propellants to elastomer B could be significant.

TABLE 4

ABSORPTION OF ISODECYL PELARGONATE AND
DIBUTYL PHTHALATE BY POLYMERS AT $60^{\circ}C$

IDP		DBP	
Low - less than 10 per cent	High - 20 per cent and over	Low - less than 10 per cent	High - 20 per cent and over
Cellulose acetate	Polyurethane rubber	Cellulose acetate	Ethyl cellulose*
Filled flexible polyester	Ethyl cellulose*	Rigid Polyester	Filled flexible polyester
Rigid polyester	CTPB*	Elastomer A	Polyurethane rubber*
Nitrile rubber	Elastomer A	Butyl rubber	CTPB*
Substituted polyolefine	Butyl rubber	Polyolefine	Neoprene*
Elastomer B	Neoprene*	Substituted polyolefine	Nitrile rubber
	Polyolefine (17)	Polyolefine copolymer	Crosslinked polyolefine
	Polyolefine copolymer*		Modified polyvinyl-acetate copolymer
	Crosslinked polyolefine		Polystyrene*
	Modified polyvinyl-acetate copolymer*		Elastomer B*
	Polystyrene		

*Absorption 100 per cent or more.

3   CONCLUSION

Polymers selected for use in solid propellant rocket motors should have only
low absorption of mobile ingredients likely to be present, particularly of
plasticisers since they may be present in quantity in the propellant.   A
maximum of 5 to 10 per cent plasticiser absorption is preferable, whilst,
above 20 per cent, absorption failure becomes progressively more likely with
increasing interaction on hot storage.   Excessive migration can give storage
lives at $60^{\circ}C$ as low as two weeks for completely unsuitable systems.
Tables 2 and 4 indicate those materials considered unsuitable for specific
plasticisers.

4   REFERENCE

1   Shipton M   Unpublished MOD(AS) Report

5 ACKNOWLEDGEMENTS

S No 49/72/BS

EFFECT OF PROPELLANT FORMULATION
SANDWICH TESTS
PLASTICISED CELLULOSE ACETATE AT 60°C

FIG 1

FIG 2 EFFECT OF BARRIER LAYERS SANDWICH TESTS-PLASTICISED CELLULOSE ACETATE AT 60°C

FIG 3

EFFECT OF FILLERS - SANDWICH TESTS -
PLASTICISED FILLED CELLULOSE ACETATE AT 60°C
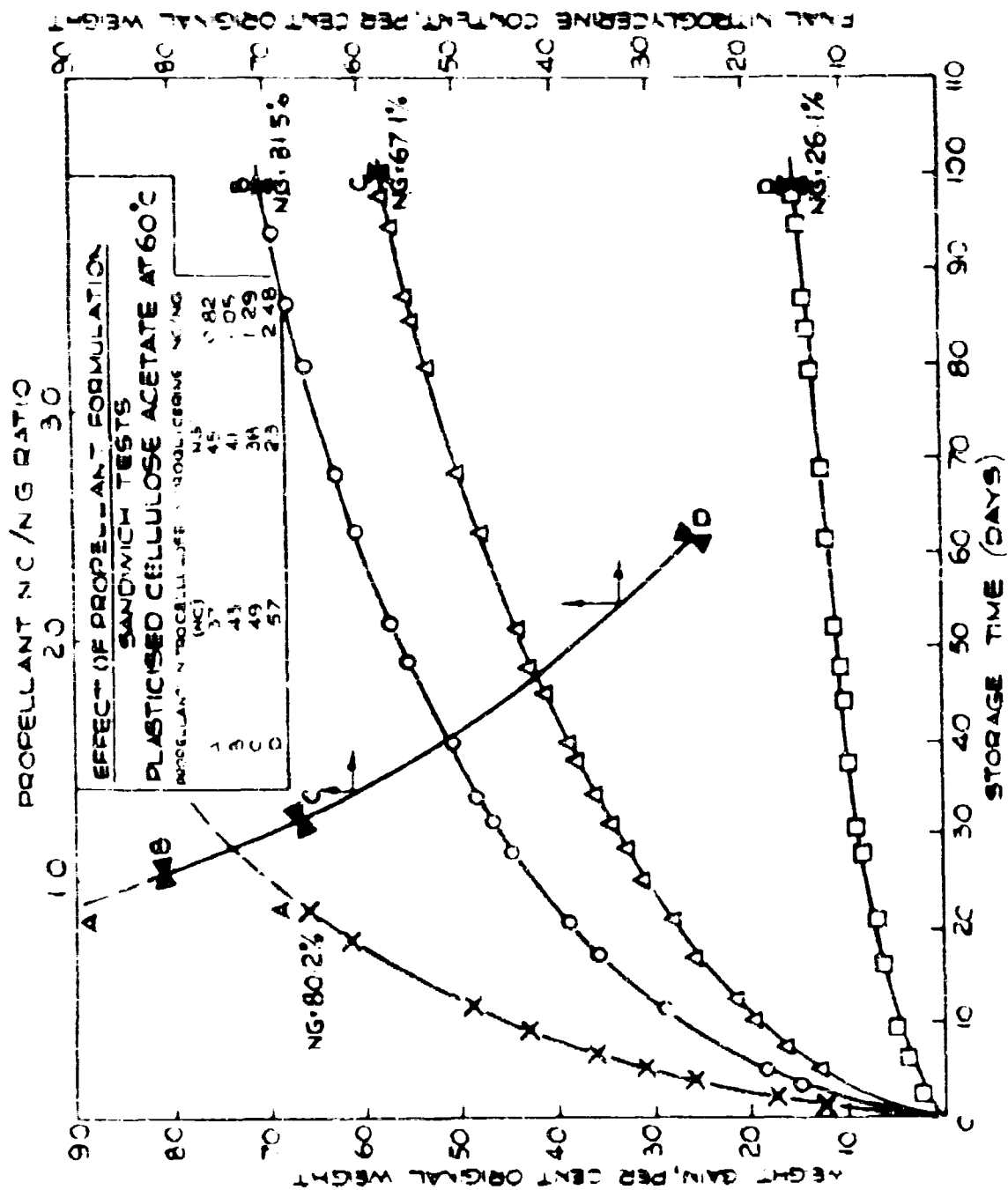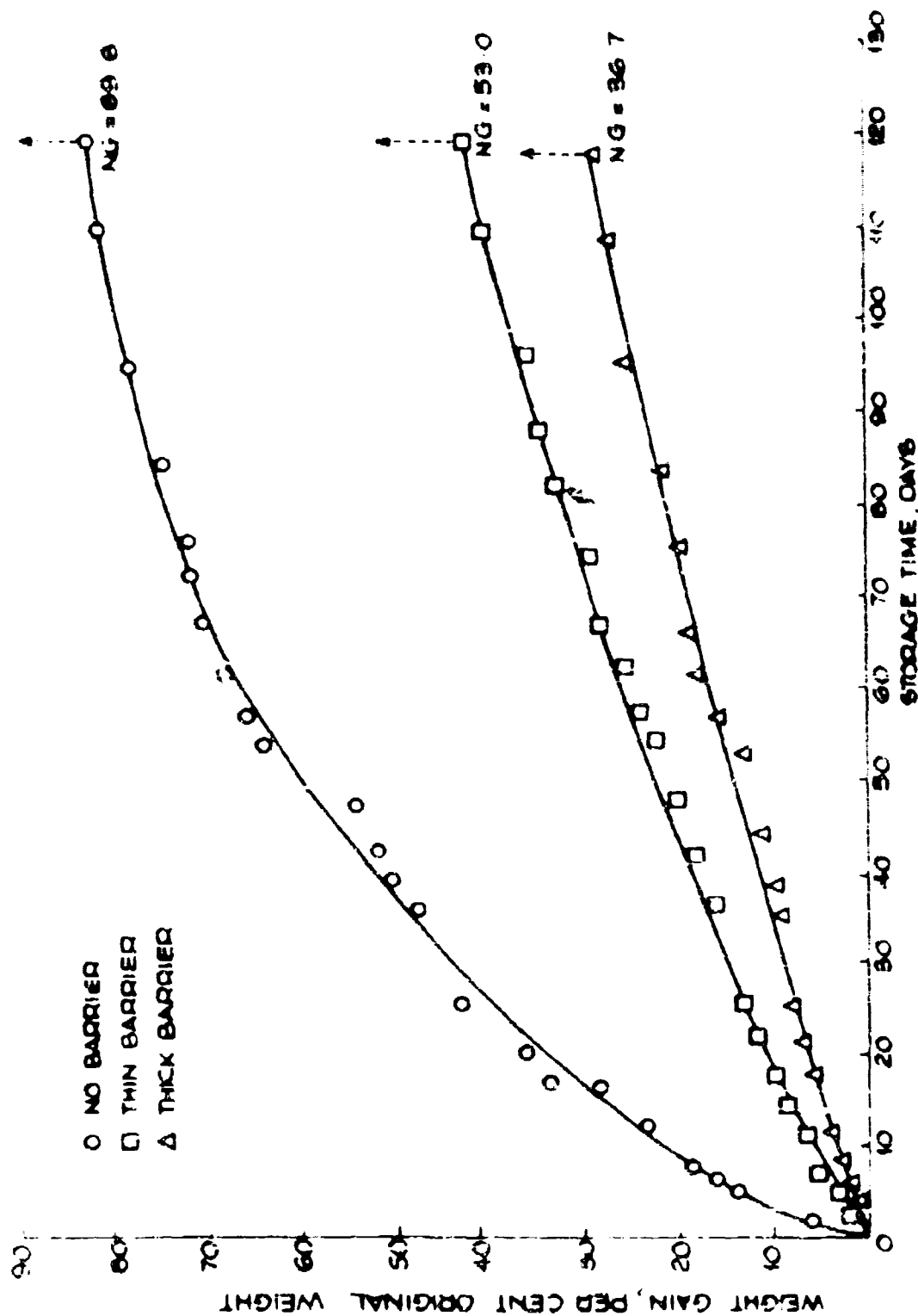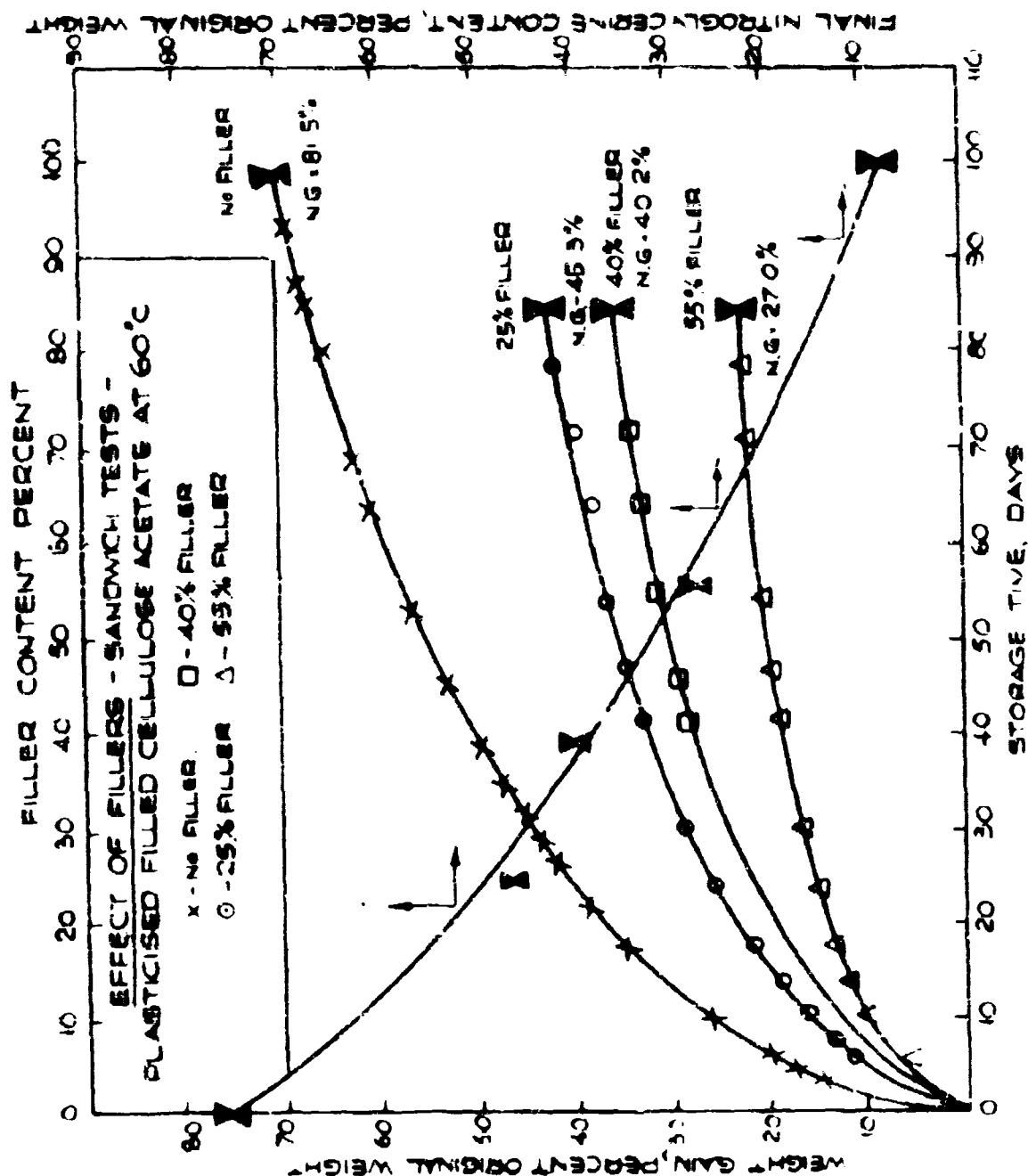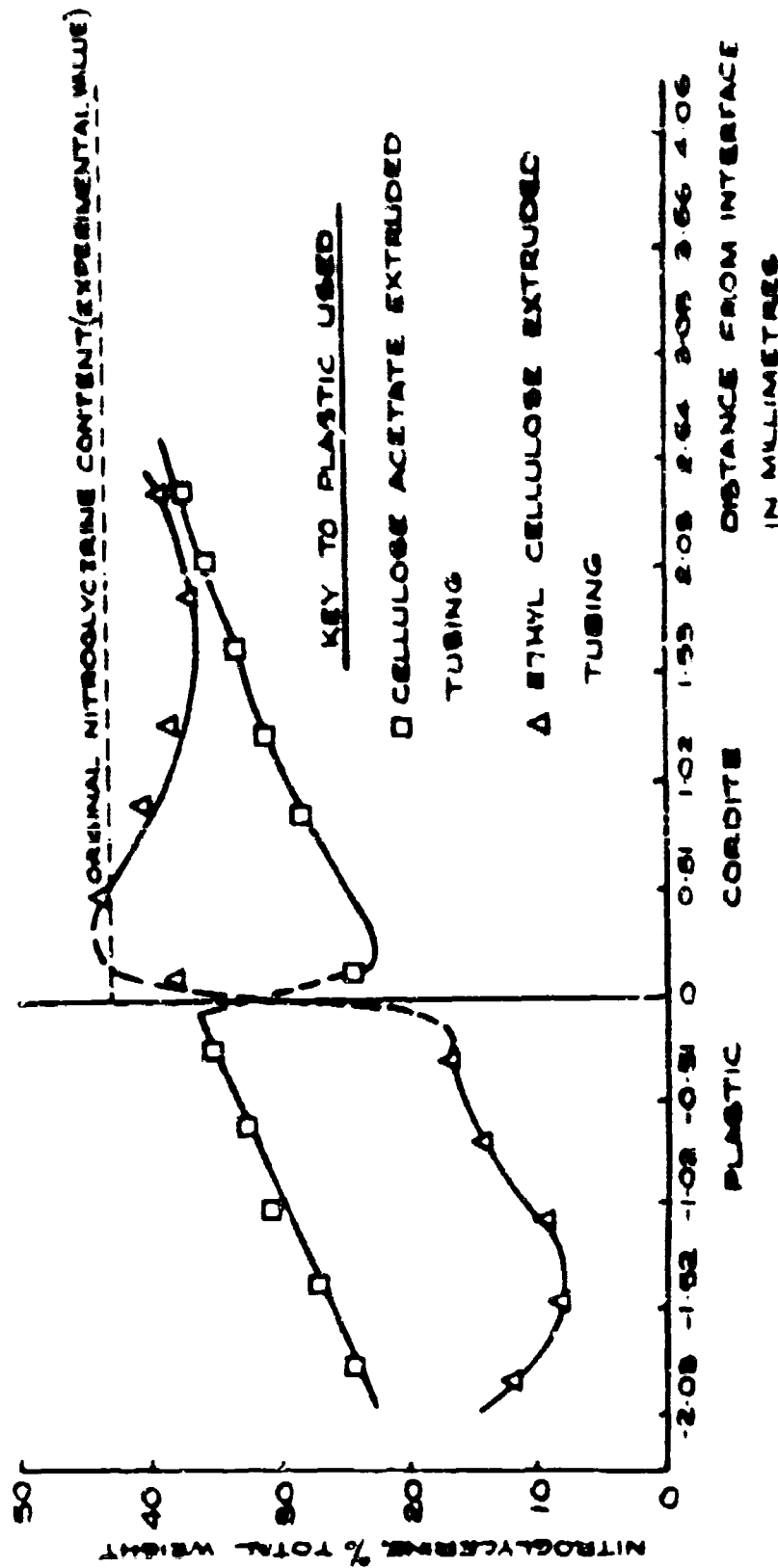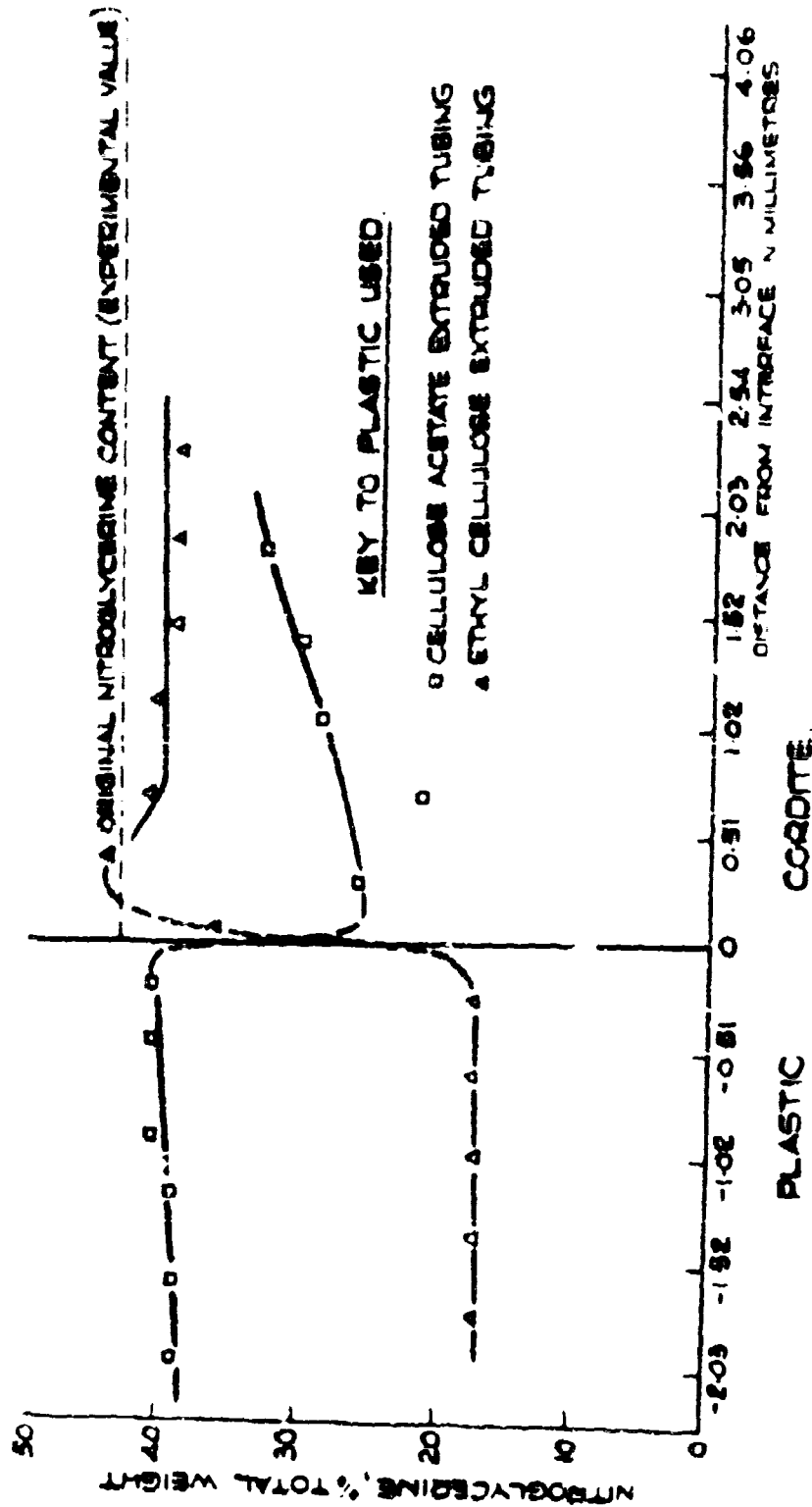
FIG 4 NITROGLYCERINE DISTRIBUTION IN CYLINDRICAL SPECIMENS AFTER

4 WEEKS AT 45°C

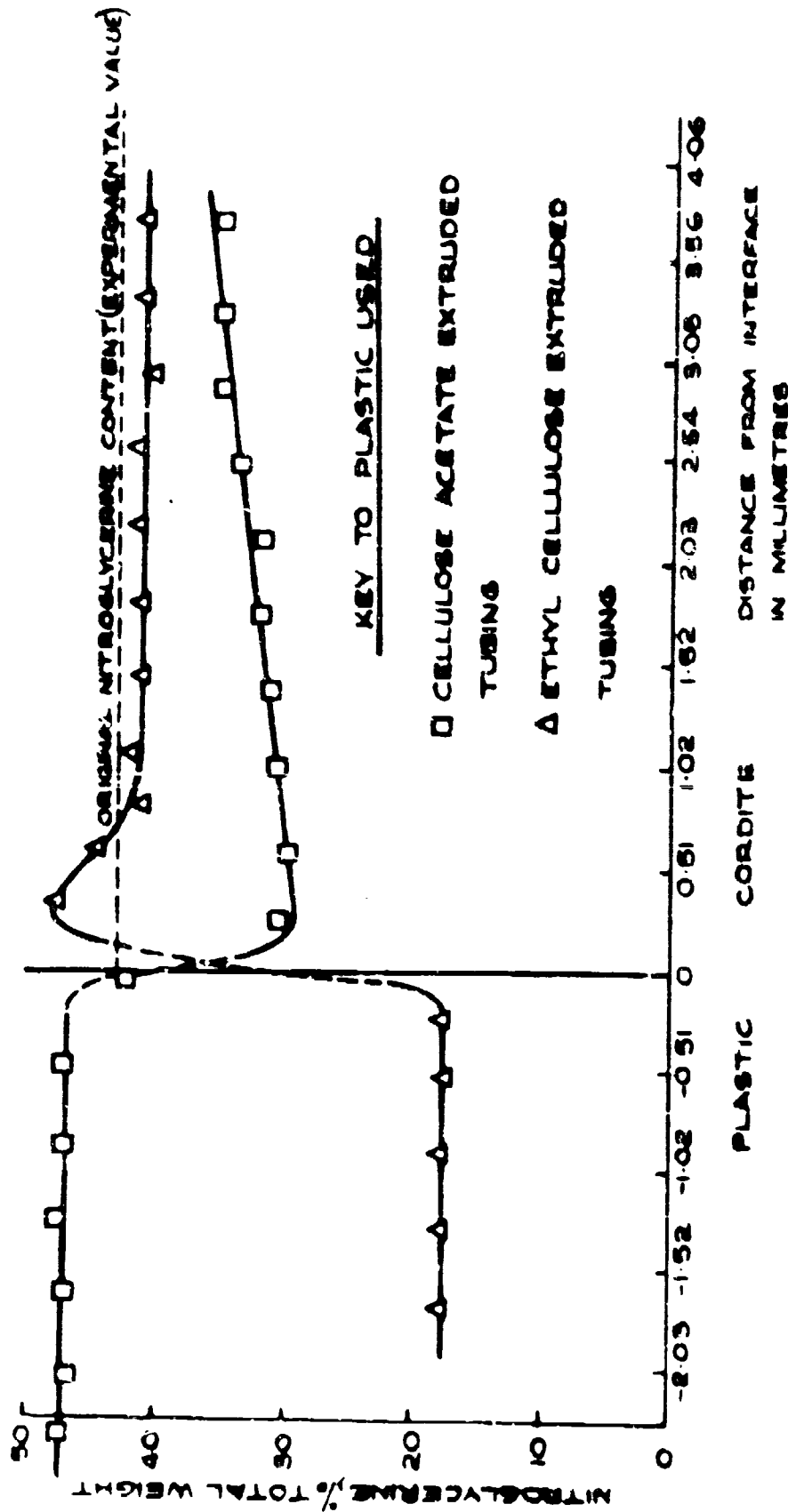FIG 5 NITROGLYCERINE DISTRIBUTION IN CYLINDRICAL SPECIMENS AFTER 11 WEEKS AT 54.5°C

KEY TO PLASTIC USED

☐ CELLULOSE ACETATE EXTRUDED
   TUBING

△ ETHYL CELLULOSE EXTRUDED
   TUBING

FIG. 6 NITROGLYCERINE DISTRIBUTION IN CYLINDRICAL SPECIMENS AFTER 26 WEEKS

AT 54.5°C

FIG 7 INERT PLASTICISER DISTRIBUTION IN CYLINDRICAL SPECIMENS AFTER 26 WEEKS AT 54.5°C

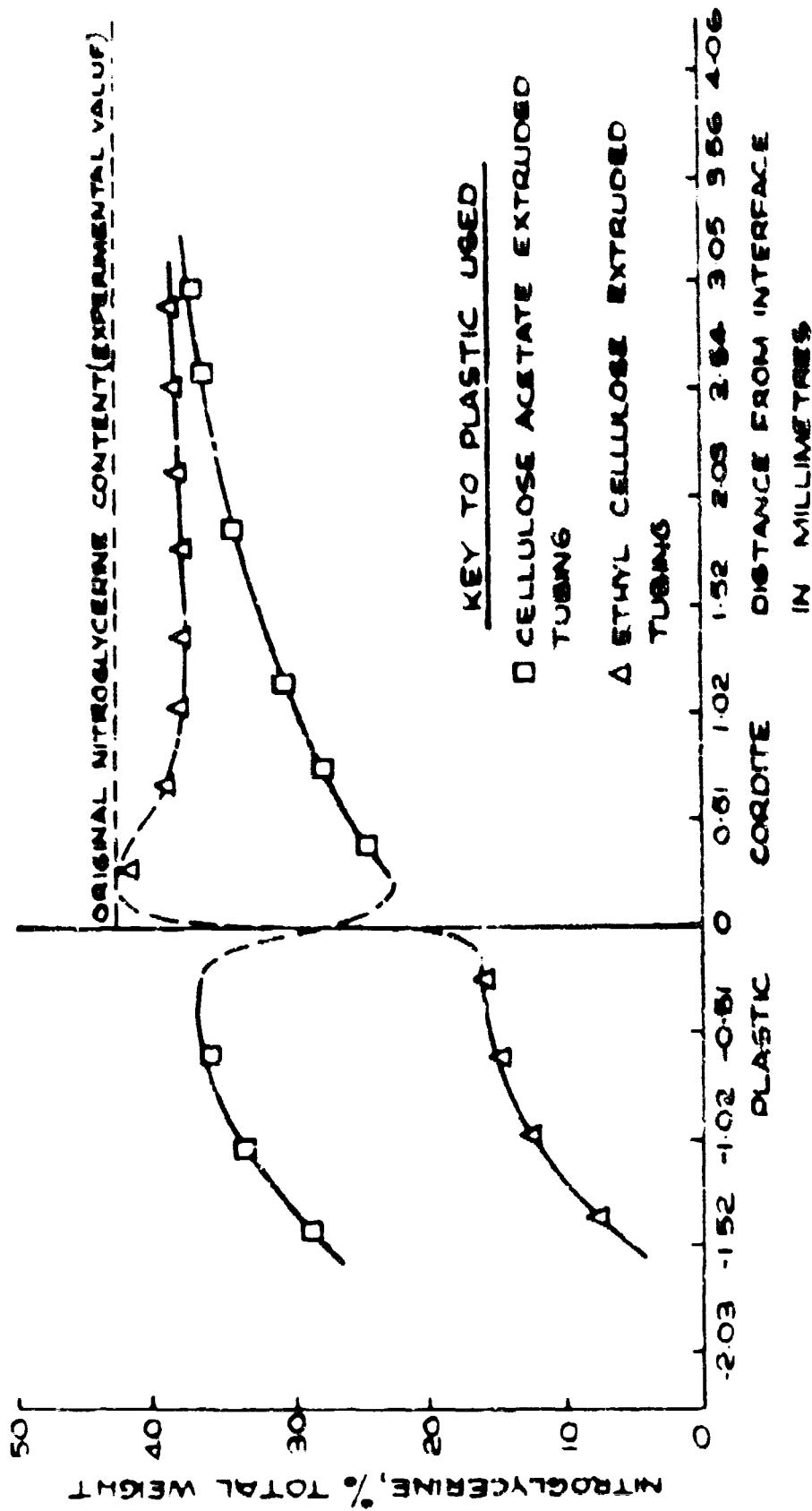FIG. 9 NITROGLYCERINE DISTRIBUTION IN COATED CHARGES AFTER 4 WEEKS

AT 54.5°C

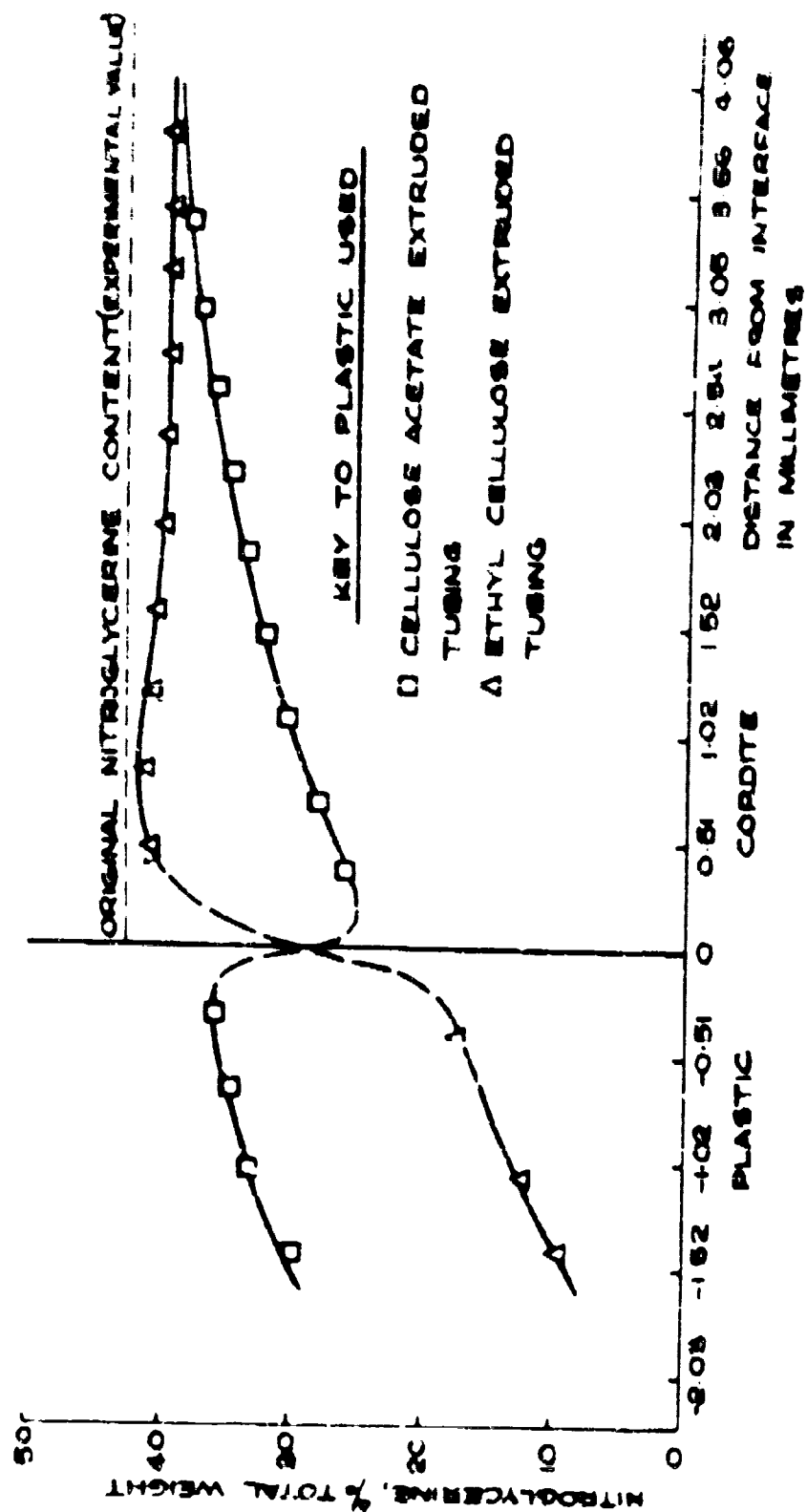FIG. 9 NITROGLYCERINE DISTRIBUTION IN COATED CHARGES AFTER 12 WEEKS

AT 51.5°C

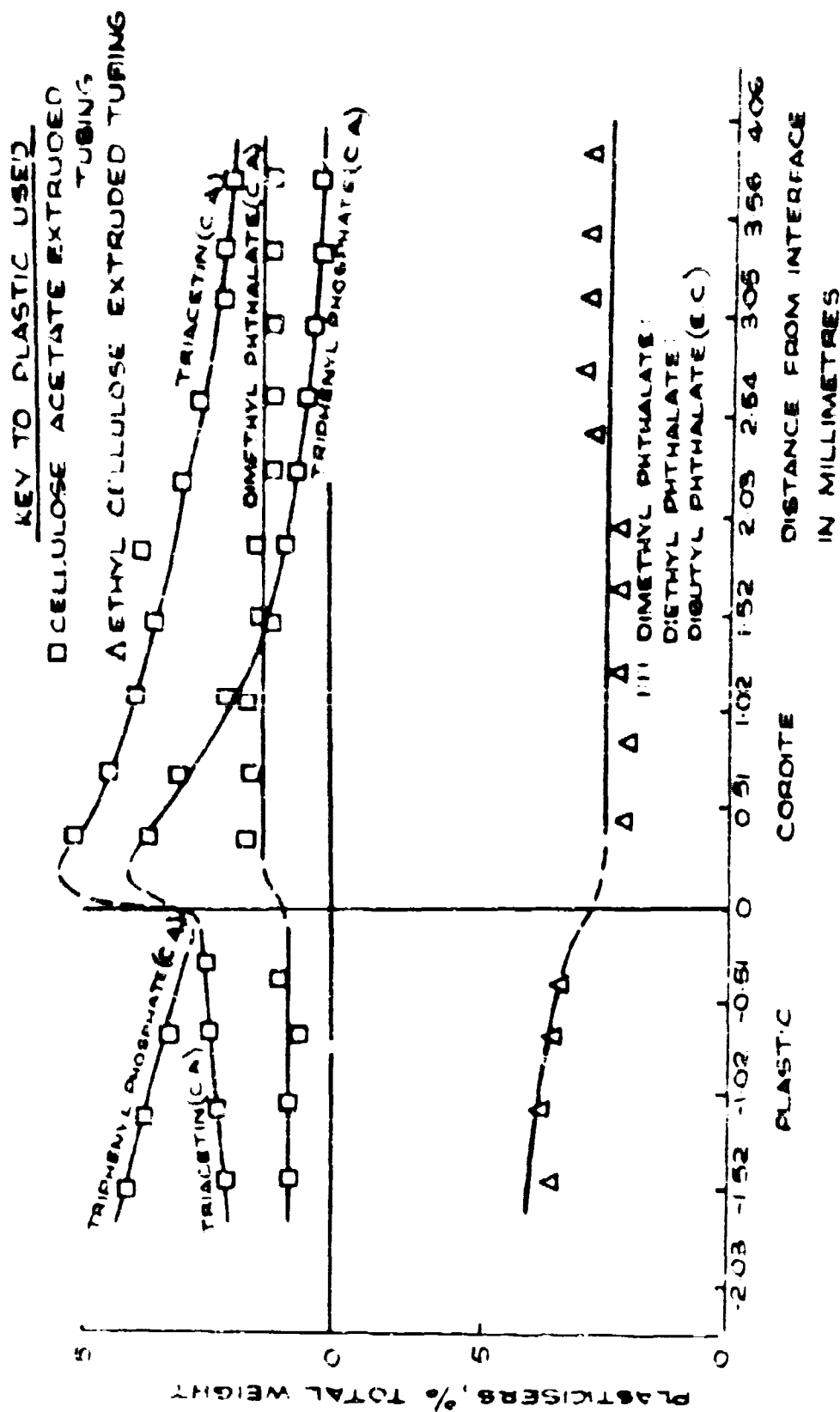FIG.10 NITROGLYCERINE DISTRIBUTION IN COATED CHARGES AFTER 26 WEEKS
AT 54.5°C

FIG 11 INERT PLASTICISER DISTRIBUTION IN COATED CHARGES AFTER 26 WEEKS

AT 54.5°C